(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number
WO 2004/005189 A1

(51) International Patent Classification[7]: C01B 33/14, 33/141

(21) International Application Number: PCT/US2003/021407

(22) International Filing Date: 10 July 2003 (10.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

10/193,025	10 July 2002 (10.07.2002)	US
60/407,413	30 August 2002 (30.08.2002)	US

(71) Applicant (*for all designated States except US*): **LANEWOOD INC.** [PA/US]; 6150 Yarrow Drive, Suite A, Carlsbad, CA 92009 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **GUTIERREZ, Ricardo** [PA/PA]; 77th Street, San Francisco, Placa Marina No. 2, Apt. 2B, Panama City (PA). **RZUCIDLO, Eugene** [US/US]; 885 Thrid Avenue, New York, NY 10022 (US).

(74) Agents: **SUTTON, Paul, J.** et al.; Greenberg Traurig, LLP, 885 Third Avenue, New York, NY 10022 (US).

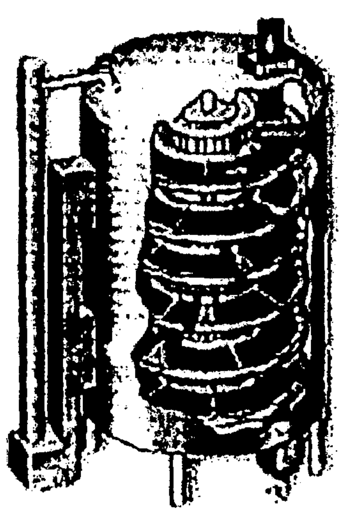
(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A STABLE AQUEOUS DISPERSION OF MICROSILICA



(57) Abstract: A stable aqueous dispersion of processed microsilica, useful as a synthetic cementitious admixture, for either increasing the maximum strength, resistance and durability of concrete or decreasing the amount of cement required to produce concrete with the same strength, resistance and durability of Portland type dry mix cements is disclosed. Figure 1 depicts a partially broken away vertical isometric view of a heater/mixer reactor for use in carrying out the process of the present invention.

WO 2004/005189 A1

A STABLE AQUEOUS DISPERSION OF MICROSILICA

BACKGROUND OF THE INVENTION

There are approximately 210 cement plants in the U.S.A. alone and the Portland Cement Association estimates that U.S. cement consumption has averaged between 75 and 90 million tons per year during the last decade. Worldwide, cement production exceeded 1.25 billion tons in 1991, according to the U.S. Bureau of Mines.

It takes about 1.75kg of raw materials to produce 1kg of finished cement, according to the Environmental Research Group at the University of British Columbia. Cement production is one of the most energy intensive of all industrial manufacturing processes. Including direct fuel use for mining and transporting raw materials cement production takes about 6 million Btus for every ton of cement (based on Portland Cement Association, 1990 data). The industry's heavy reliance on coal leads to especially high emission levels of carbon dioxide, nitrous oxide and sulphur. Most of the energy consumed is for operating the rotary kilns.

In the U.S.A. for the approximately 80 million tons of cement used in 1992, roughly 0.6% of total energy used in the U.S.A. was required. Cement represents only about 0.06% of G.N.P. illustrating its energy intensiveness. According to the World Watch Institute, in some third world nations cement production accounts for as much as two-thirds of total energy consumption.

Cement admixtures are common to the cement industry. The amount of cement admixtures available in the industry are legion. They are typically used to impart characteristics to the concrete mix that are required for a specific purpose, i.e. expedited hardening, increased resistance, etc. Generally, these cement admixture preparations are designed to be used with Portland cement, the standard for the industry.

Portland cement is perhaps the most popular type of cement used today due to its high strength, relative impermeability and durability, particularly in its ability to withstand highly moist, acid rain, or even continuously wet conditions. Portland cement is distinguishable by the presence of a relatively high proportion of calcium oxide, in addition to the silicon dioxide and alumina present in most sands. In general, a conventional Portland cement will contain approximately 60 to about 67% by weight of calcium oxide, from about 17 to about 25 percent

by weight of silica dioxide, 3 to 8 percent by weight of alumina, 0.5 to 6 percent by weight of iron oxide, 0.1 to 4 percent by weight of magnesia (MgO), and soda and/or potash ($Na2O$, $K2O$) in amounts of about 0.5 to 1.3 percent by weight. Generally, Portland cement particulates are smaller than 100 microns (as for example measured by a Coulter counter) with an average particle dimension of at least one micron but generally less than about 75 microns.

Many modern cements use Portland cement as a base but also include materials that function as pozzolans. Pozzolans are generally siliceous or siliceous/aluminous materials in extremely finely divided form, so as to have an immense surface area per unit volume or weight. Pozzolans classically have been obtained from, for example, volcanic ash, pumicites, opaline cherts, shales, tuffs, and certain diatomaceous earths.

Preferably, synthetic pozzolans have been obtained as by-products from other industrial processes, such as silica fume, fly ash, or finely-ground slag. Generally, the most preferred pozzolans will include a high proportion of amorphous, finely-divided silicon. For example, silica fume, also known as condensed silica fume or microsilica, is a by-product material from the production of ferro-silicon or silicon metal, has a sub-micron particle size, i.e., a particle size of generally not greater than about 0.2 microns, an extremely low bulk density and extremely large surface area. To remove impurities, such as substantial proportions of carbon from unburnt coal (especially from the ferro-silicon processes), as well as a certain amount of elemental silicon, such by-products are often further treated so as to provide a higher purity silica. Silica fume most useful in admixtures with Portland cement is at least about 90% by weight amorphous silica. The silica fume has been added in amounts up to 100% of the weight of the other components of the cement. For ease of handling, dry microsilica is often 'densified', which reduces bulk density and surface area, but leaves a product which can readily be changed back to the original properties of microsilica when admixed, e.g., into a cement paste. Microsilica has also previously been slurried with water, for the same reasons.

The densified microsilica is generally also purified to remove any carbon material that may remain as the by-product from the manufacture of ferro-silicon or of silicon metal, and to increase particle size and bulk density. Silica fume, as condensed, has a bulk surface area of at least about 20,000 m^2/kg. of particles, the densified product, about one-third that value. The material used should contain at least about 80% and preferably at least about 90 % silicon-dioxide, and most preferably over 92% by wt. In practicing the present invention there can be

used either the original extremely fine silica fume particles or the preferred and more easily and safely processed densified microsilica particles. This agglomerated densified microsilica formed by densification breaks up to reform the microsilica particles during mixing

When the term "concrete" is used herein, it is intended to also encompass what is often called "mortar", which is distinguished primarily by the maximum size of the aggregate present in the concrete and bound together by the cement. Mortar comprises generally smaller aggregates with a maximum dimension of approximately 2 to 4 millimeters. Generally, this encompasses sand. What is commonly called "concrete" includes as the aggregate larger particle size pebbles, generally referred to as gravel.

Concretes from such pozzolanic cements have greater impermeability as well as greater compressive strengths. For example, silica fume has been found to be extremely useful in increasing resistance to sulfate and sea water attack when added to Portland cement. It has been theorized that this increased resistance is the result of the removal from the set concrete of free calcium hydroxide, as a result of its combination with the pozzolanic material.

In addition to the silica fume or processed micro silica other compounds having the following activity have been found to be useful in cement admixtures: accelerators; retarders; water reducers; air entraining agents ; polymer-modified systems and deflocculating agents. Further details regarding these compounds may be found in the CONCRETE ADMIXTURES HANDBOOK, SECOND EDITION, V.S. Ramachandran (ed.), (Noyes Publications, New Jersey, 1995).

Portland cement is the most expensive component in concrete formation. Therefore, there is continually ongoing research regarding means of decreasing cement usage in the production of concrete and concrete products. Generally, this research attempts to search for admixtures that will enable the production of the same volume of substantially equal strength concrete while decreasing the cement content. This problem is especially acute in the circumstance where concrete blocks or other concrete prefabricated products (of generally low water content) are being manufactured, but also exists with respect to the in situ laying of concrete.

Many inventors have attempted to devise methods of forming a stable aqueous slurry of microprocessed silica to be added *in situ*. However, to date, all of these methods require additions of other agents, most frequently water reducing agents, or continuous mixing to

stabilize a silica slurry to prevent the settling or hardening of the slurry that prevents efficient transportation to the worksite.

SUMMARY OF INVENTION

The present invention provides a cement admixture composition comprising a stable suspension of a microfine particulate pozzolan, such as silica fume or microprocessed silica, in an aqueous formaldehyde solution. In a preferred embodiment, there may also be mixed into the suspension, prior to adding to a cement paste, additional ingredients, such as silica in the form of fine sand, particulate calcium oxide, water reducing agent, corrosion inhibitor, retarding agent and/or magnesium oxide, among other materials that will not interfere with the stability of the suspension of the microsilica. The addition of the stable aqueous dispersion of fine particles of microsilica to a cement paste enables its user to either produce concrete that has increased maximum strength, resistance and durability, or alternatively, to decrease the amounts of cement required without reducing the same strength, resistance and durability of Portland type dry mix cements. A comparatively small amount of the product of this invention added to the water of the cement paste or mortar allows a reduction of the amount of cement used to manufacture such products of at least about 15% up to about 40%. Alternatively, if the cement concentration in the final product is not reduced, this invention increases maximum strength, impermeability and durability of the finished concrete product.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood from reading the following description of non-limiting embodiments, with reference to the attached drawings, wherein below:

FIG. 1 depicts a partially broken away vertical isometric view of a heater/mixer reactor for use in carrying out the process of the present invention;

Fig. 2 depicts a vertical view of a distillation column for use in carrying out the process of the present invention; and

Fig. 3 depicts a condenser known in the art, for use in carrying out the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the process of the present invention, the stable aqueous dispersion is formed by the admixing of the microfine particulate silica, having an average particle size of not greater than about 0.75μ, and preferably not greater than 0.5μ, with an aqueous liquid to create a viscous homogenous slurry, which will be referred to as "diluted micro-silica" (or "DMS"). After being thoroughly mixed, the DMS is passed into a heated mixer, and maintaining substantial homogentity preferably with slow mixing (up to about 300 rpm, but generally, at least about 50 rpm,) at an elevated temperature preferably below its boiling point, and most preferably at a temperature above about 75° C, until the mixture forms an aqueous gel. Thereafter, the mixing shear is increased, e.g., by increasing the speed of the mixing blades to greater than about 300 rpm (but generally not above about 600 rpm), so as to break down the gel and form a stable aqueous dispersion of fine particulate silica, i.e., of microsilica particles. Preferably, the elevated temperature of the aqueous gel is maintained during the entire procedure. The resultant stable aqueous dispersion of processed microsilica is a fluid, pourable, stable suspension which can replace a far larger quantity of Portland Cement in a concrete paste mixture, while maintaining the same desirable properties, or maintain the same quantity of cement and provide a concrete having improved strength, impermeability, and durability.

In accordance with a preferred aspect of the present invention, the aqueous liquid is a dilute aqueous formalin solution. The formalin solution that is most preferably utilized in preparing the diluted processed microsilica is a diluted formaldehyde/water solution, wherein the theoretical saturated solution of formalin (37% by wt. of formaldehyde gas, or 40 grams of formaldehyde per 100 ml. of solution) is diluted with water (optimally distilled water), in an amount of from about 10% to about 50%, and most preferably from about 20 to about 40%, by total wt. of the aqueous liquid. Most preferably, the dilute aqueous formalin solution contains at least about 20% by weight of formaldehyde, and optimally at least about 25% by wt.

The fine particulate silica can be mixed in an amount of up to about 100% by wt., or even greater, of the aqueous liquid, e.g., formaldehyde solution. However, the concentration of the microsilica in the slurry is to be determined by the use to which it is to be put. Generally, in order to limit the volume of liquid suspension shipped, the fine particulate silica

is present in an amount of at least about 10% by wt. of the aqueous liquid. The maximum amount is limited only by the stability of the suspension and the particular use to which it will be put, including the other components to be added.

Generally, when preparing a stable aqueous dispersion of the pozzolan in accordance with this invention, for use for the *in situ* formation of, e.g., structural support members in the construction of buildings or roadways, the preferred concentration of the, e.g., fine particulate silica, is in the range of from about 10% by wt. of the aqueous liquid up to about 40% by wt. of the aqueous liquid; when the term "aqueous liquid" is used in this context, it refers to the disperse medium, e.g., the dilute aqueous formaldehyde solution. Generally, when preparing a stable aqueous dispersion of the pozzolan in accordance with this invention, for use in concrete paste that will be used to produce blocks of concrete or other prefabricated concrete products, in a factory context, the preferred concentration of the, e.g., fine particulate silica, is in the range of from about 30% by wt. of the aqueous liquid up to about 80% by wt. of the aqueous liquid. As stated above, this invention is particularly effective with Portland cement compositions.

The resultant product is a free flowing, fluid, and stable aqueous dispersion which can be admixed with conventional Portland cement in a concrete paste to provide concrete having improved strength, impermeability and durability when exposed to inclement, wet or corrosive conditions.

The stable aqueous dispersion of the microsilica is preferably mixed with other additives when intended for use as a cementitious additive. Depending upon the particular use to which it will be put, for the formation of concrete, the preferred concentration of the microsilica will also change. For example, when adding the dispersion to a concrete paste to be used in the in situ pouring of concrete, for example in road building or building bridge construction, the microsilica is present in an amount preferably not greater than about 50% by wt. of the aqueous liquid, and most preferably not greater than about 40%. When using the dispersion for the factory manufacturing of, e.g., concrete blocks or prefabricated structural components, where the concrete paste usually has a lower proportion of water, the microsilica is preferably present in greater quantities, up to about 80% by wt.

Similarly, other components will vary depending on the use. For example, when used for so-called *in situ* pouring of concrete, the dispersion can preferably also contain a water reducer, such as a lignosulfonic acid; a fine particulate silicon dioxide sand; a naphthalene-

containing water-reducer, such as a commercially available naphthalene lignosulfate mixture; and particulate calcium oxide. When being used as a cementitious additive for a concrete paste being utilized in the factory manufacturing of prefabricated concrete products, the dispersion can preferably contain a higher proportion of the microsilica, and any of the following additives commonly used for such manufacturing, including a water reducer and/or superplasticizer, including sulfonated naphthalene formaldehyde condensates, sulfonated melamine formaldehyde condensates, refined or unrefined lignosulfonic acid derivatives, hydroxycarboxylic acids and combinations thereof; accelerators, such as calcium chloride, calcium formate, sodium sulfate; corrosion inhibitors, such as magnesium and zinc fluosilicates or carbonates; and an oxide of magnesium or calcium.

In accordance with the present invention there is now provided a stable aqueous dispersion of processed microsilica which functions as a cementitious admixture manufactured from low-cost components, which are combined in accordance with a process and in a composition that is significantly different and provides improved compressive strength and reduced permeability in concrete made therewith. By the use of the stable aqueous dispersion of microsilica of the present invention, the proportion of cement and water in the concrete mixture can, if desired, be substantially reduced overall without loss of compressive strength, or the strength can be dramatically improved, while maintaining the same proportions of materials, or some combination of the two achieved by intermediate changes in composition.

To produce the stable aqueous dispersion of microsilica of this invention the following preferred process can be used. In this description, all components of the invention are expressed as percentages of the total weight of the final product, unless expressly indicated otherwise. To an aqueous formaldehyde solution is added, with mixing, microsilica or condensed silica fume, to create a viscous homogenous slurry, which will be referred to as "diluted micro-silica" (or "DMS"). The microsilica can be of equal weight to the aqueous liquid into which it is mixed. After being thoroughly mixed, the DMS is passed into a heated mixer, and maintained with slow mixing, at an elevated temperature preferably about 75° C and below its boiling point, until the mixture forms an aqueous gel. Thereafter, the temperature of the aqueous gel is maintained, but the shear on the gel is increased by increasing the speed of the mixing blades, e.g., to greater than about 300 rpm, so as to break down the gel and form a stable aqueous dispersion of microsilica particles. The resultant

stable aqueous dispersion of processed microsilica is a fluid, pourable, stable dispersion which can replace a far larger quantity of cement in a concrete paste mixture, or maintain the same quantity of cement and provide a concrete having improved strength, impermeability, and durability.

In accordance with a most preferred aspect of the present invention, the processed micro-silica, or silica fume, is mixed into a dilute formalin solution in a mixer operating at a speed of up to about 150 rpm, to create the DMS. The thoroughly mixed DMS is passed into a heated mixer, of the type depicted in Figure 1, where the DMS is then heated to between about 80°C and 90°C while the mixing blade operates at a speed of up to about 300 rpm, but most preferably below about 150 rpm, until an aqueous gel is formed. The aqueous gel is then maintained at an elevated temperature in the heater-mixer, but greater shear is applied by increasing the mixing speed, e.g., to greater than about 300 but most preferably not above about about 600 rpm, so as to break down the gel and form a stable aqueous dispersion of microsilica.

In a most preferred procedure, the stable aqueous dispersion is then transferred to a still that includes a blade mixer, and preferably provides substantial refluxing, using the condenser depicted in Figure 3, so as to obtain a final liquid density preferably greater than about 1.16 but not greater than about 1.19 g/cc. (most preferably between about 1.17 and about 1.18) and pH of at least about 6 (most preferably of between about 6 and about 7). The resultant product is a free flowing, fluid, and stable aqueous dispersion which can be admixed with conventional Portland cement in a concrete paste to provide concrete having improved strength, impermeability and durability when exposed to inclement, wet or corrosive conditions.

Use of the stable aqueous dispersion of the pozzolan in accordance with this invention can result in substantial increase in compressive strength and impermeability of a standard Portland cement based concrete. It has been found moreover, that the invention is most effectively used in combination with other components, premixed before addition to the concrete paste mix. The particular components that are to be added, and the precise composition, depends on the final use for the concrete paste. Specifically, the composition which generally has the most beneficial effect for use with concrete paste mixes to be mixed and poured in the field, as for the *in situ* molding of structural concrete in construction projects, or the building of roads, is generally different from the compositions used for the

factory manufacturing of, e.g., prefabricated concrete structures or the manufacture of concrete blocks.

Alternatively, a significant cost savings, without loss of the desirable characteristics of the standard Portland concrete, can be achieved by reducing the quantity of Portland cement by from about 15 up to about 40 percent by wt. of the total, and reducing the water:cement ratio, and adding the stable aqueous dispersion of microsilica product of the present invention. This is accomplished without sacrificing the workability of the fresh, wet concrete mixture, and without any loss of the desirable slump of the concrete mixture. In addition, there is a significant reduction in the presence of undesirable air bubbles brought into the mixture during the mixing operation of the concrete material or during pouring of the mixture into the construction site molds. Generally, the synthetic aqueous dispersion of the present invention is added at a ratio of between about 8 and about 14 ounces per hundred pounds of the cement, i.e. Portland cement.

Tests, well known and standard in the concrete industry, have been performed whereby the effects of the invention on various indices of concrete strength and durability have been assessed. These tests confirm that significant advances have been made and the resultant concrete has either increased strength and durability when the invention is added to standard amounts of Portland cement or the same strength and durability can be had with decreases of Portland cement of up to 40% per unit of concrete.

The equipment used in the preparation of the invention is well known to one of skill in the art. A glass lined heater/drier is preferably employed in several of the steps described above, i.e. a unit with a 2000 Gallons capacity is commercially available from Pfaudler, Inc. of Rochester New York, USA. This heater/drier is depicted in Figure 1, herewith. The mixer blade depicted is generally described as a curved blade turbine, such as is commercially available from Pfaulder Inc., under the designation "Curved Blade Turbine". The concentrating still, as depicted in Figure 2, includes a propeller mixer in the lower pot for maintaining sufficient mixing during the distillation. The condenser for the still of Figure 2 is depicted in Figure 3.

The stable dispersion of this invention can be admixed with several other components, either prior to shipment or *in situ*, without affecting the stability of the aqueous dispersion. Any number of well known cement additives may be employed in their normal capacity including, but not limited to, water reducers and/or superplasticizers, such as sulfonated

naphthalene formaldehyde condensates, sulfonated melamine formaldehyde condensates, refined or unrefined lignosulfonic acid derivatives, hydroxycarboxylic acids and combinations thereof; accelerators, such as calcium chloride, calcium formate, and sodium sulfate; corrosion inhibitors, such as magnesium and zinc fluosilicates or carbonates; oxides calcium or magnesium oxide or other Group II metals; and larger particle size silicon dioxide.

The stable aqueous dispersion of the present invention can be readily added to a concrete paste mixture in almost any desired amount. It has been found to be useful to add sufficient dispersion so as to provide at least about a dosage of from about 8 fluid ounces to about 14 fl.ozs., and preferably 10 to about 13 fl.oz., per 100 pounds of cement in a concrete mixture. The synthetic liquid cementitious liquid admixture of this invention can be used with most types of cement, including for example, Portland Cement, Blended Hydraulic Cements, White Portland Cement and Expansive Cements, with or without pozzolan content.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples described preferred embodiments of the present invention and are not meant to limit the scope of the invention in any manner.

EXAMPLE 1

In the manufacture of 1 gallon of the desired synthetic cementitious aqueous dispersion, 18.15 fl.oz. of distilled water are admixed with 30.91 fl.oz. of formalin solution (i.e., a 37% by wt. formaldehyde gas solution). Into this liquid is added 2.67 lbs. of processed microsilica having a particle size with an average range of 0.1μm sold under the tradename Boral Ultra Pozz by Boral Material Technologies. This mixing to form the DMS is accomplished using a Rotomix® propeller mixer manufactured by Admix Inc. operating at a speed of about 100 rpm.

This diluted microsilica is then passed to a glass lined heater/drier, as depicted in Figure 1, heated to 85°C and mixed with a blade rotational speed of 150 rpm. The diluted microsilica liquid is maintained at that temperature for 30 to 35 minutes with continued mixing at the end of which the composition gels. The gelled composition continues to be heated at the same temperature but the rotational speed of the mixing blades are increased to about 450 rpm. The product, a stable aqueous dispersion of microsilica, is obtained within about 25 to about 40 minutes, comprising 46% by wt. of the microsilica based on the total weight of the dispersion product.

EXAMPLE 2

The aqueous dispersion of Example 1 can be taken directly from the heater/dryer and then passed directly to a still, where it is heated to its boiling point (above 90° to below 100°C), while being mixed with a propeller mixer. When the average density has reached a value of 1.174 g/ml., the aqueous dispersion of processed microsilica is transferred from the bottom of the still to a heater/drier, where the stable aqueous dispersion of processed microsilica, is maintained at a temperature of about 85°C and mixed at a blade speed of 150 rpm for at least 20 minutes. The following components are then added to the dispersion: Glycolic Acid, 17.91 fl.ozs., as sold by Dupont CAS # 79-14-1, E.I. du Pont de Nemours and Co.; Magnesium and Zinc Fluosilicate, 14.45 fl.ozs., Magnesium Fluosilicate, CAS #18972-56-0 supplied by Luciem Chemical Industries and Zinc Fluosilicate CAS #1687171-71-9 ,

supplied by BASF Belgium SA/NV; and Magnesium Oxide, 5.56 ozs., CAS #1309-48-4, having an average particle size of 5 microns, manufactured by Martin Marietta Magnesia Specialities LLC, and sold under the trade name Mag Chem 35. The resulting combined product is a stable aqueous dispersion that functions as a synthetic cementitious admixture that can be stored at room temperatures for an extended period without gelling, agglomerating, or precipitating. Further, this particular embodiment has been found to be particularly useful in concrete mixtures used in the production of prefabricated concrete structures and concrete blocks, which generally require a lower proportion of water.

About 8 fl.ozs. to about 10 fl.ozs. of the synthetic cementitious liquid admixture, prepared above, is added to 100 lbs. of Portland Cement to obtain prefabricated concrete products exhibiting a 5000 PSI when tested at 28 Days.

The Cement used in the above concrete composition is a commercially available product identified as Rinker Portland Cement Type 1, as sold by Florida Materials, and contains the usual calcium aluminate silicate powder. When mixed and tested, the resulting concrete showed at least a two-fold increase in compressive strength, as compared to concrete made from the same Portland Cement composition, without the addition of the liquid synthetic cementitious product of this invention.

In another test, about 10 fl.ozs. of the synthetic cementitious liquid admixture, is added to a concrete paste containing 70 lbs. of Portland Cement. The amount of water used to mix the concrete paste can be reduced, as compared to the standard compositon prepared without adding the liquid synthetic cementitious composition of this invention, without adversely affecting the compressive strength of the product.

EXAMPLE 3

In the production of 10 gallons of an embodiment of the present invention, 392 ounces of distilled water are admixed with 128 ounces of formalin solution (i.e., a 37% by wt. formaldehyde gas solution). Into this liquid is added 8.2 pounds of processed microsilica having an average particle size of 0.1 μm, sold under the tradename Boral Ultra Pozz by Boral Material Technologies. This mixing forms the dilute microsilica slurry, and is accomplished using a Rotomix® propeller mixer manufactured by Admix Inc. operating at a speed of about 100 rpm.

This diluted microsilica slurry is then passed to a glass lined heater/drier, as depicted in Figure 1, heated to 85°C and mixed with a blade rotational speed of 150 rpm. The diluted

microsilica liquid is maintained at that temperature for 30 to 35 minutes with continued mixing at the end of which the composition gels. The gelled composition continues to be heated at the same temperature but the rotational speed of the mixing blade is increased to about 450 rpm. An aqueous dispersion is obtained during this process within about 25 to about 40 minutes. The aqueous dispersion from the heater/dryer is then passed to a still and heated to its boiling point, above 90 to below 100°C), while being mixed with a propeller mixer. The resultant stable aqueous dispersion is useful in the present form as an admixture in the production of concrete that requires a normal water:cement ratio, and is useful in the *in situ* pouring of concrete, as in road building.

EXAMPLE 4

The aqueous dispersion of Example 3 can be taken directly from the heater/dryer and then passed directly to a still, where it is heated to its boiling point (above 90° to below 100°C), while being mixed with a propeller mixer. When the average density has reached a value of 1.174 g/ml., the aqueous dispersion of processed microsilica is transferred from the bottom of the still to a heater/drier, where the stable aqueous dispersion of processed microsilica, is maintained at a temperature of about 85°C and mixed at a blade speed of 150 rpm for at least 20 minutes. The following components are then added to the dispersion: lignosulfonic acid, 182.6 fl. ozs.; silicon dioxide powder, 13.3 pounds (98.6% SiO_2 having an average particle size of 10μm, commercially available as Min-U-Sil 10, sold by US Silica Company); napthalene lignosulfate solution, 146.9 fl. ozs., as sold by Hill Brothers Chemical Co.; and pulverized calcium oxide, 83 pounds, having a particle size of 200 mesh 99.9%, commercially identified as Quick Lime Pulverized Rotary (RPQL) Calcium Oxide, as sold by Mississippi Lime Co. The resulting stable aqueous admixture product may be stored at room temperatures for an extended period without gelling, agglomerating, or precipitating.

The stable aqueous dispersion of the present example, (91 fl. oz.) is combined with the following Portland Cement Composition:

Cement (Portland Mix)	650 lbs
Sand (commercial fine)	1200 lbs.
Gravel	2200 lbs.
Water	28 Gals.

The Cement used in the above concrete composition is a commercially available product identified as Rinker Portland Cement Type 1, as sold by Florida Materials, and contains the usual calcium aluminate silicate powder. When mixed and tested, the resulting concrete showed at least a two-fold increase in compressive strength, as compared to concrete made from the same Portland Cement composition, without the addition of the liquid synthetic cementitious product of this invention.

The composition of Example 4 was prepared by adding 77 fl. ozs. of the aqueous dispersion liquid synthetic cementitious product described above to 550 lbs. of Portland Cement, and the quantity of water was reduced by 20%, to 22.4 Gals. The resultant concrete had substantially the same compressive strength as the standard composition prepared without adding the liquid synthetic cementitious composition of this invention.

The above description of the invention is merely exemplary of the preferred embodiments of the invention. The scope of the invention is defined by the following claims.

What is claimed is as follows:

1. A stable aqueous dispersion of fine particulate pozzolan comprising an aqueous liquid and microsilica dispersed in the liquid.
2. A stable aqueous dispersion according to claim 1, wherein the composition contains densified microsilica.
3. A stable aqueous dispersion according to claim 1, wherein the microsilica comprises from about 5 to about 60% of the total weight of the aqueous dispersion.
4. A stable aqueous dispersion according to claim 1, further comprising materials selected from the groups consisting of Group II metal oxides, concrete-water reducing agents, air entraining agents, and corrosion inhibitors selected from Magnesium and Zinc Fluosilicates.
5. A stable aqueous dispersion according to claim 1 further comprising a fine particulate sand.
6. A stable aqueous dispersion according to claim 1, wherein the aqueous liquid is a formalin solution.
7. A process for preparing a stable aqueous dispersion of a fine particulate pozzolan, the process comprising: mixing microsilica with an aqueous liquid to create a homogenous slurry; heating the slurry to an elevated temperature to form a gel; and shearing the gel so as to form the stable aqueous dispersion.
8. The process of claim 7, wherein the aqueous liquid is a formalin solution.
9. The process of claim 8, wherein shearing the gel comprises mixing the gel with a mixing blade rotating at a speed of at least about 300 rpm while maintaining the gel at an elevated temperature.

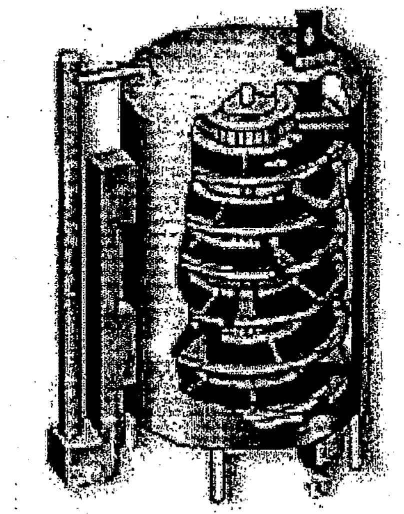


FIG. 1

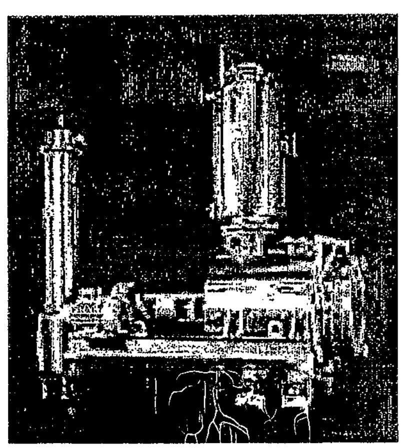


FIG. 2

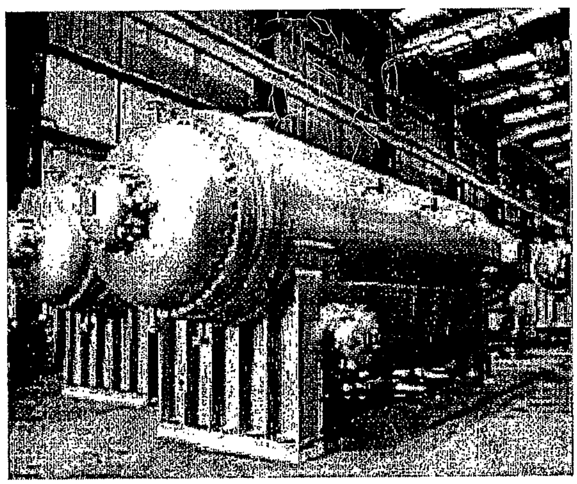


FIG. 3

INTERNATIONAL SEARCH REPORT	International application No. PCT/US03/21407

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 33/14, 33/141
US CL : 106/482, 423/335; 516/81

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 106/482, 423/335; 516/81

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,321,243 A (CORNWELL et al.) 23 March 1982, abstract, examples and claims.	1-4
X	US 4,888,058 A (ROSENBERG et al.) 19 December 1989, abstract, examples and claims.	1-4
X	US 5,116,535 A (COCHRANE) 26 May 1992, abstract, examples and claims.	1-3
X	US 5,246,624 A (MILLER et al.) 21 September 1993, abstract, examples and claims.	1-4
X	US 5,332,041 A (ONAN et al.) 26 July 1994, abstract, examples and claims.	1-4
X	US 5,438,083 A (TAKIMOTO et al.) 01 August 1995, abstract, examples and claims.	1-4
X	US 5,514,211 A (MARKS et al.) 07 May 1996, abstract, examples and claims.	1-4
X	US 6,074,987 A (SHAFER et al.) 13 June 2000, abstract, examples and claims.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 September 2003 (03.09.2003)	02 OCT 2003

Name and mailing address of the ISA/US	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703)305-3230	Anthony J. Green Telephone No. 703-308-0661